National Aeronautics and Space Administration

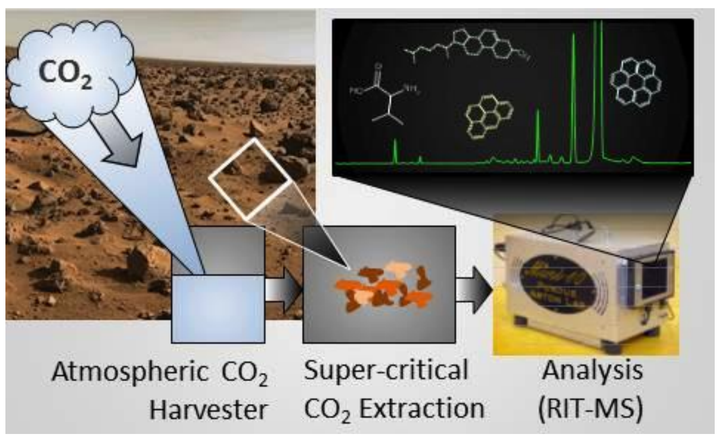
Extraction of Amino Acids Using Supercritical Carbon Dioxide for *in Situ* Astrobiological Applications

Isik Kanik, Marlen Menlyadiev, Bryana L. Henderson, Fang Zhong, and Ying Lin

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

Overview

Mars In-Situ Organic Detection Instrument Using Supercritical CO_2 (SCCO2) Extraction



The detection of organic molecules that are indicative of past or present biological activity on Mars is a key research activity in astrobiology. To date, space missions to Mars have primarily used pyrolysis technique to extract organic compounds from the Martian regolith but it has not enabled a clear detection of unaltered native Martian organics. The elevated temperatures required for pyrolysis extraction can cause native Martian organics to react with perchlorate salts in the regolith, possibly resulting in the chlorohydrocarbons that have been detected in earlier missions to Mars.

Supercritical carbon dioxide ($SCCO_2$) extraction technique is a powerful alternative to pyrolysis that may be capable of extracting and delivering unaltered native organic species to an analyzer. In this study, we report the $SCCO_2$ extraction of unaltered amino acids (AAs) with laboratory analysis of extracts by capillary electrophoresis laser-induced fluorescence (CE/LIF) and liquid chromatography mass spectrometry (LC/MS) techniques.

Major Project Goals

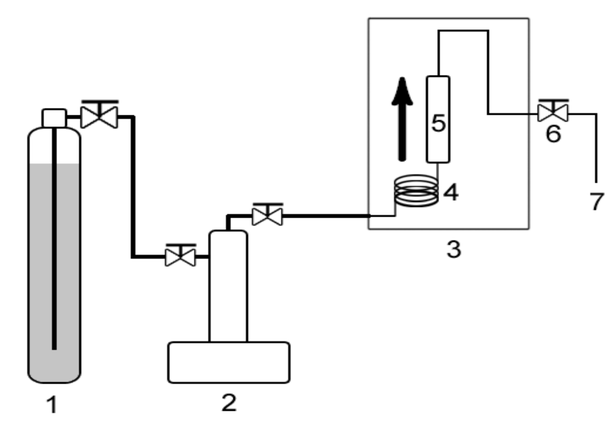
- Harvest CO_2 from Martian atmosphere.
- Extract organics under gentle SCCO2 conditions to prevent thermal degradation or reaction with native perchlorate salts.
- Analyze extracts with mass spectroscopy.
- Extract and detect compounds at ppb to ppt level.

Challenges of In-Situ Organic Analysis

- Pyrolysis-based extraction methods require elevated temperatures.
- Perchlorate salts are present in Martian regolith at ppth level.[1]
- Organics may degrade in the presence of perchlorates at elevated temperatures.[2,3]
- Native organics may not be identified.[4]

Supercritical CO_2 Extraction

Benchtop Extractor: Proof of Concept Experiments

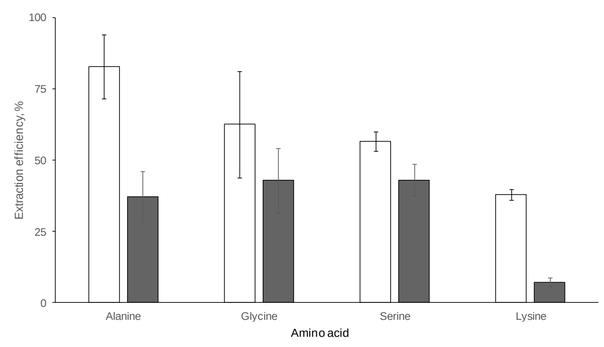


SCCO2 extraction system diagram:

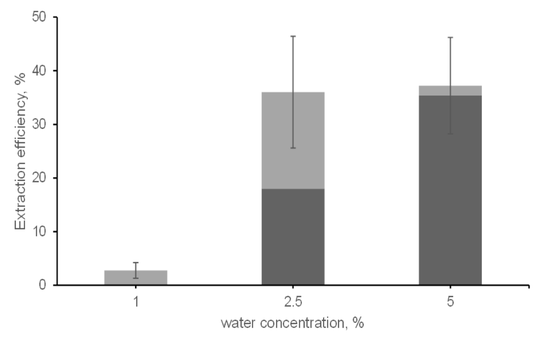
CO2 is supplied from a cylinder of liquid CO2, (1), that is equipped with a regulator. Syringe pump, (2), supplies high pressure CO2. The oven, (3), maintains extraction cell at desired temperature. (4) CO2 passes through coiled tubing to bring it up to oven temperature. (5) Sample is loaded into the extraction cell, (5), and SCCO2 flows upward through the sample as indicated by the arrow. The restrictor valve controls flowrate at the outlet, (7).

Extraction Efficiency of Amino Acids

Extraction Efficiency of some of the representative of Amino Acids

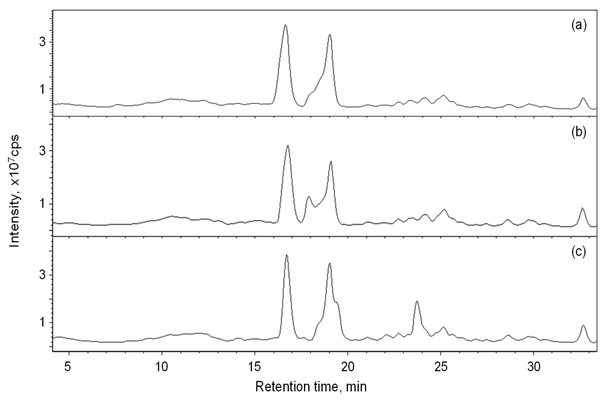


Extraction efficiencies of some of the representative amino acids (smallest, with non-polar, polar and basic side chains) on their extraction efficiencies from glass beads (white bars) and JSC Mars-1A Martian regolith simulant (dark bars; P= 2800 psi, T= 75˚C H_2O concentration= 5% and concentration of each amino acid is 50 ppm).

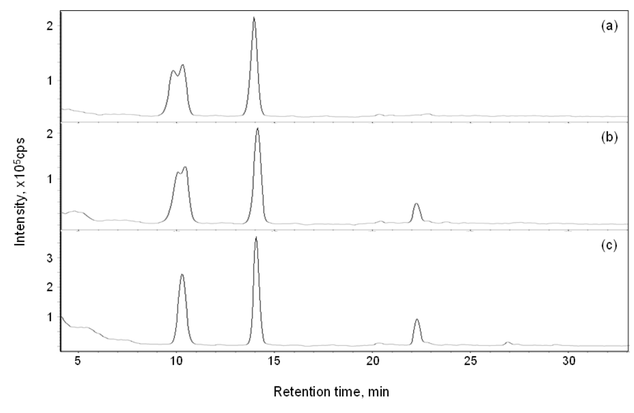


Effect of the water concentration on the extraction efficiency of 50 ppm of alanine from JSC Mars-1A Martian regolith simulant (P= 2800 psi, T= 75˚C). The darker part of the bar indicates the portion of extracted alanine which was collected during the dynamic extraction step in the collection test tube, while light part corresponds to extracted alanine which deposited out on the walls of the transfer line and was later washed out the line for analysis

Extraction of Amino Acids from JSC Mars-1A Martian Regolith Simulant



LC/MS analysis of three extracts of JSC Mars-1A Martian regolith simulant: (a) pure $SCCO_2$ extract, (b) $SCCO_2$/5% H_2O extract and (c) pure H_2O extract (P= 2800 psi, T= 75˚C H_2O concentration 0, 5% or 100%, respectively).

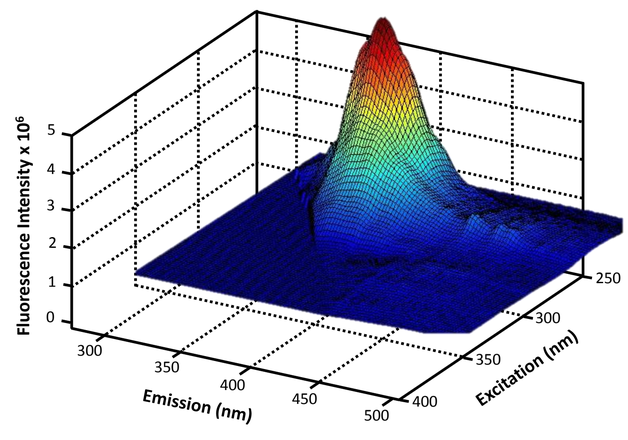


Extracted ion chromatograms (XICs) at m/z 400 from LC/MS analysis of three extracts of JSC Mars-1A Martian regolith simulant: (a) pure $SCCO_2$ extract, (b) $SCCO_2$/5% H_2O extract and (c) pure H_2O extract (P= 2800 psi, T= 75˚C H_2O concentration 0, 5% or 100%, respectively).

Extracting Native Compounds

A Step Towards Complex Samples

- 3D fluorescence spectra of JSC Mars-1 extracted with SCCO2.
- Suggests extraction of native compounds at sub-ppb level.
- Indicates SCCO2 may be able to extract native, sub-ppb level organics from Martian regolith.
- May be more difficult to achieve with real Martian regolith if compounds are strongly bonded to the dirt.



Conclusions

- Extracted a variety of organic compounds with pure SCCO2.
- Perchlorate does not hinder extraction nor degrade extracted amino acids.
- Possible extraction of trace native organics from Martian regolith simulant.
- Experiments indicate that SCCO2 extraction may overcome some of the challenges revealed by previous in situ organic analysis on Mars.

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Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

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